FIRST PRINCIPLES BASED REACTIVE ATOMISTIC SIMULATIONS TO UNDERSTAND THE EFFECTS OF MOLECULAR HYPERVELOCITY IMPACT ON CASSINI'S ION AND NEUTRAL MASS SPECTROMETER. A. Jaramillo-Botero[1] [ajaramil@caltech.edu], M-J Cheng[1], V. Cvicek[1], Luther W. Beegle[2], R. Hodyss[2], and W.A. Goddard III[1] [wag@wag.caltech.edu], [1]California Institute of Technology, 1200 E California Blvd, Pasadena, CA 91125, [2]Jet Propulsion Laboratory, California Institute of Technology 4800 Oak Grove Drive, Pasadena, CA 91109.

Introduction: NASA's Cassini Cassini's Ion and Neutral Mass Spectrometer (INMS) has returned a wealth of data on the composition of Titan's upper atmosphere and the plumes of Enceladus. However the encounter velocity (up to 17.73 km/sec) of the spacecraft with the plume or atmosphere has profound effects on the fragmentation of the observed molecules. Measured compositional changes of H_2O, H_2, CO_2 and CO appear to be correlated with velocity (see Figure 1). To understand this phenomenon, we have applied first principles based atomistic methods to simulate the physics of hypervelocity impacts of organic and inorganic molecules on metal surfaces. These methods include non-adiabatic and adiabatic reactive molecular dynamics calculations designed to elucidate the relationship between impact energy, fragmentation efficiency and fragmentation pathways. We report here on the predicted impact of species such as ice-water, CO_2, CH_4, and NH_3, on oxidized titanium, as well as HC species on diamond surfaces. These simulations provide the dynamics of product distributions during and after a hypervelocity impact event, ionization fractions, and dissociation probabilities for the various species of interest as a function of impact velocity (energy). We are using these results to determine the relevance of the fragmentation process to Cassini INMS results, and to quantify its effects on the observed spectra.

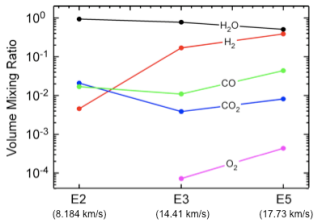

Figure 1 *Changes in the measured composition of the Enceladus plume as a function of encounter velocity[2]*

The Ion and Neutral Mass Spectrometer (INMS): The INMS is a quadrupole mass spectrometer equipped with two separate ion sources, the closed source and the open source. Data on the composition of the Enceladus plumes and the upper atmosphere of Titan has primarily been obtained with the closed source, whose operation we will briefly describe.

The closed source is made up of a spherical titanium antechamber which is connected to a hot filament electron impact ionizer by means of a transfer tube[1]. The ionizer fragments and ionizes the incident molecules before they are focused in the quadrupole for mass analysis. The fragmentation patterns are an important means of identifying the parent molecules, and an accurate knowledge of these is necessary to deconvolute the overlapping peaks that result from the mixture of gases entering the mass spectrometer. Gas enters the antechamber through the entrance aperture, and is thermalized through collision with the antechamber walls before entering the ionizer. This arrangement achieves a ram enhancement of the gas pressure in the antechamber above that of the ambient gas, due to the high velocity of the spacecraft relative to the ambient gas[1].

At Enceladus, spacecraft encounter velocities range from about 8 km/s (E2 encounter) to 14.41 km/s (E3) to as high as 17.73 km/s (E5)[2]. The encounter velocity with Titan on 26 October 2004 was ~ 6 km/s[3]. The fundamental physical properties of hypervelocity molecular collisions, such as fragmentation patterns as a function of impact energy, are largely unknown for the species of relevance to INMS. This data must be obtained for a proper analysis of the INMS spectra.

Reactive molecular dynamics: Recent breakthroughs at Caltech, namely, the first-principles-based electron force field (eFF)[4-6] and the first-principles-based ReaxFF reactive force field[7-10] provide an unprecedented opportunity for accurately describing the energetics and molecular fragmentation phenomena of the atmospheric and plume species during hypervelocity impact with INMS chamber walls.

ReaxFF provides nearly the accuracy of ground state quantum mechanics (QM) for describing reactive processes at computational costs comparable to conventional non-reactive force fields. The functional forms in ReaxFF give accurate descriptions of transition states for allowed and forbidden reactions, consisting of bond order dependent valence terms, environmentally dependent charge distributions [11], and non-bond or van der Waals (vdw) interactions between all atoms. All ReaxFF parameters are fit directly to QM descriptions of reactions, equations of state, and other thermodynamic and geometric information, resulting in highly transferable potentials. We have validated ReaxFF on numerous reactive systems[7, 8, 10].

It is the combination of simulating reactivity, diffusion, material decohesion, and phase transitions that enables an accurate description of complicated chemical events associated with varying temperature gas-

phase reactions, surface chemistry, transport and flow of reactive species across the INMS surfaces and interfaces; within an adiabatic approximation.

To study the non-adiabatic effects of electronic excitations on the dynamics of impact (e.g. electron ionization) we developed the electron force field (eFF) method. With eFF, electrons are explicitly included in the dynamical equations, but instead of solving the time-dependent Schrödinger equation, we write the many-electron wavefunction as a Hartree product of floating Gaussian wavepackets, one for each electron, and propagate the dynamics as the electrons and nuclei interact, while allowing these Gaussian wavepackets to expand and contract dynamically. We use a spin dependent potential to replace the orthogonality induced by the Pauli principle, allowing nonadiabatic transitions to be described in calculations that scale nearly linearly with size. eFF has just three universal scaling parameters (for the spin dependent Pauli interactions), yet it leads to reasonable geometries and energies for molecules containing atoms with covalent, ionic, multicenter, or metallic bonding

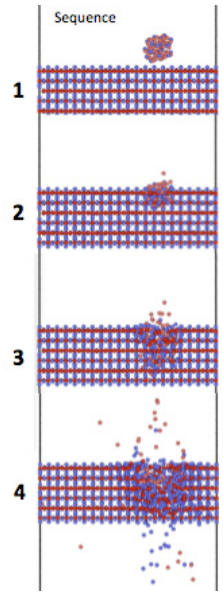

Figure 2 $31H_2O$ *ice cluster impacting* TiO_2 *at 25km/s damages the INMS surface. (ReaxFF).*

Simulations Setup. A ReaxFF force field was prepared from QM (DFT-B3LYP level) for handling Ti/O/H/C interactions, including TiO_2 bulk and (110) surface, CO_2, liquid and ice H_2O, and numerous hydrocarbons (including CH_4, C_2H_6, C_6H_6, $C_5H_{10\text{-}12}$, and C_6H_{14}). Molecular structures corresponding to the target TiO_2 surface and impactor species were prepared, optimized and thermally equilibrated at 100K, before running hypervelocity impacts at varying speeds, 5 to 25km/s, using an NVE dynamics ensemble with 0.25 fs timesteps in ReaxFF. Explicit electron structures corresponding to a diamondoid surface (with and w/out H coverage) target and saturated hydrocarbon species impactors were also prepared and run in the same manner with eFF. Both, ReaxFF and eFF, cases were run over the LAMMPS framework.[12]

Simulation Results. Using ReaxFF we studied the surface mechanics and kinetics during impact of an Ice-I cluster structure against the TiO_2. Ice impact at 25km/s leads to perforation of a thin 6-layer TiO_2 film (see Figure 2), producing among other species H, O_2, O, H_2, Ti, and TiO. No water molecules remain after impact. Ti atoms are exposed by impact and released onto the surface, increasing its reactivity.

For most other species, the consistent pattern involves few or no reactions at 5km/s impacts, species adsorption by the TiO_2 surface at 10km/s, and increased fragmentation at higher velocities, with predominant products being CO, H_2, OH, H, and some water molecule, confirmed by data received from the Cassini spacecraft.

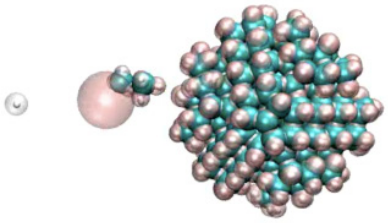

Figure 3 *eFF simulation of a methane molecule impacting an H-covered diamondoid surface at 20km/s shows fragmentation due to valence electron ionization (large red sphere).*

Our eFF results with small hydrocarbons (C_2H_6 and CH_4) impactors on a diamond surface show valence electrons ionizing and leading to C-H bond breaking above 15km/s for the H-capped diamond case, and at lower velocities for the H-uncapped surface, consistent with experimental findings. C_2H_6 is adsorbed by surface for impact velocities >=25km/s.

Concluding remarks: This work is improving our understanding of the physics and chemistry of hypervelocity collisions of molecular species with Cassini's INMS, providing an opportunity for decoding the existing data captured from the different mission flybys over Saturn' moons. This has broad applicability across the Saturnian system, including Titan, Enceladus and Saturn's rings. Improvements in the interpretation of INMS data will have a positive effect on complementary data from other Cassini instruments, such as the Visual and Infrared Mapping Spectrometer (VIMS) and the Composite Infrared Spectrometer (CIRS).

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